



-2-naphthol-4-sulfonic acid) indicator: This changes from red through purple to bluish purple to a pure blue without any trace of red or purple tint. The pH of some waters must be raised to 14 (rather than 12-13) by the use of 8 N NaOH in order to get a good color change. Grind in a mortar 200 mg powdered dye and 100 g solid NaCl to 40 to 50 mesh. Store in tightly stoppered bottle. Use 0.2 g of this mixture for titration.

- 5.3 Standard EDTA titrant, 0.02 N: Place 3.723 g analytical reagent grade disodium ethylenediamine tetraacetate dihydrate,  $\text{Na}_2\text{H}_2\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$  in a 1 liter volumetric flask and dilute to the mark with distilled water. Check with standard calcium solution (5.3.1) by titration (5.3.5). Store in polyethylene. Check periodically because of gradual deterioration.
- 5.3.1 Standard calcium solution, 0.02 N: Place 1.000 g anhydrous calcium carbonate (primary standard low in heavy metals, alkalis and magnesium) in a 500 mL flask. Add, a little at a time 1 + 1 HCl (5.3.2) until all of the  $\text{CaCO}_3$  has dissolved. Add 200 mL distilled water. Boil for a few minutes to expel  $\text{CO}_2$ . Cool. Add a few drops of methyl red indicator (5.3.3) and adjust to intermediate orange color by adding 3N  $\text{NH}_4\text{OH}$  (5.3.4) or 1 + 1 HCl (5.3.2) as required. Quantitatively transfer to a 1 liter volumetric flask and dilute to mark with distilled water.
- 5.3.2 Hydrochloric acid solution, 1 + 1
- 5.3.3 Methyl red indicator: Dissolve 0.10 g methyl red in distilled water in 100 mL volumetric flask and dilute to mark.
- 5.3.4 Ammonium hydroxide solution, 3 N
- 5.3.5 Standardization titration procedure: Place 10 mL standard calcium solution (5.3.1) in a vessel containing about 50 mL distilled water. Add 1 mL buffer solution (5.3.6). Add 1-2 drops indicator (5.3.7) or small scoop of dry indicator (5.3.7). Titrate slowly with continuous stirring until the last reddish tinge disappears, adding last few drops at 3-5 second intervals. At end point the color is blue. Total titration duration should be  $\leq 5$  minutes from the time of buffer addition.

$$\text{N of EDTA} = \frac{0.2}{\text{mL EDTA}}$$

- 5.3.6 Buffer solution: Dissolve 16.9 g ammonium chloride in 143 mL conc ammonium hydroxide in a 250 mL volumetric flask. Add 1.25 g of magnesium salt of EDTA (5.3.8) and dilute to the mark with distilled water. Store in tightly stoppered plastic bottle.
- 5.3.7 Indicator: Commercially available Eriochrome Black T is used in one of the three methods described. All gradually deteriorate.
- 5.3.7.1 Mix 0.5 g dye with 4.5 g hydroxylamine hydrochloride. Dissolve in 100 mL of 95% ethanol or isopropanol.
- 5.3.7.2 Place 0.5-1.0 g dye in 100 g of triethanolamine or 2-methoxyethanol.
- 5.3.7.3 Mix 0.5 g dye and 100 g NaCl for dry formulation.

5.3.8 EDTA Magnesium Salt: Commercially available.

## 6.0 Procedure

### 6.1 Pretreatment

6.1.1 For drinking waters, surface waters, saline waters, and dilutions thereof, no pretreatment steps are necessary. Proceed to 6.2.

6.1.2 For most wastewaters and highly polluted waters, the sample must be digested as given in the Atomic Absorption Methods section of this manual, paragraphs 4.1.3 and 4.1.4. Following this digestion, proceed to 6.2.

### 6.2 Sample Preparation:

6.2.1 The calcium content of the 50 mL aliquot to be titrated should be 5-10 mg, therefore dilution should be used for high calcium concentrations.

6.2.2 If the alkalinity is > 300 mg/L CaCO<sub>3</sub> and cannot be reduced by dilution because of low calcium concentration, the alkalinity must be decreased by acidifying, boiling one minute and cooling.

### 6.3 Titration

6.3.1 Add 2.0 mL NaOH solution (5.1), or a volume sufficient to produce pH 12 to 13, to 50 mL of sample.

6.3.2 Stir. Add 0.1 to 0.2 g indicator (5.2.2 or 5.2.3) or 1-2 drops if indicator solution is used.

6.3.3 Immediately titrate with continuous stirring. Check to see that no further color change occurs when using murexide (5.2.2) by adding 1 to 2 more drops of titrant after recording milliliters of titrant at first judged end point.

## 7.0 Calculations

### 7.1 Total calcium

$$\text{mg/L Ca} = \frac{A \times N \times 20,040}{\text{mL of sample}}$$

where:

A = mL titrant

N = Normality of EDTA solution

### 7.2 Calcium hardness

$$\text{mg/L CaCO}_3 = \frac{A \times N \times 50,000}{\text{mL of sample}}$$

where A and N are the same as in 7.1.

## 8.0 Precision and Accuracy

8.1 A synthetic unknown sample containing 108 mg/L Ca, 82 mg/L Mg, 3.1 mg/L K, 19.9 mg/L Na, 241 mg/L chloride, 1.1 mg/L nitrate N, 250 μg/L nitrite N, 259 mg/L sulfate, and 42.5 mg/L total alkalinity in distilled water was

determined by this method with a relative standard deviation of 9.2% and a relative error of 1.9% in 44 laboratories.

### **Bibliography**

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 189, Method 306C (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D511-76, Method B, p 253(1976).